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EXPERIMENTAL STUDIES ON THE HYDROGEN ELECTRODE

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science of
Columbia University.

BY
LOUIS P. HAMMETT
II
NEW YORK CITY
1922

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W. A. W.

TO MY WIFE.

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It is a great pleasure to acknowledge my gratitude to Professor H. T. Beans for the initiation of this work and for his constant advice and supervision in its execution.

EXPERIMENTAL STUDIES ON THE HYDROGEN ELECTRODE

The hydrogen electrode is an instrument of such scientific importance that the lack of detailed study of its mechanism and of the conditions for precise measurements seems very remarkable. There are numerous directions for the preparation and use of the electrode¹, which in the hands of the particular investigator have given reproducible results on a given type of solution; but these are often contradictory, and there is a lack of experimental comparison of different methods. The present investigation was initiated largely by the desire to explain and eliminate the erratic and uncertain behavior of the hydrogen electrode in unbuffered solutions, but this has necessitated a general survey of the field.

Apparatus and Materials.

Electrical measurements were made with a Leeds and Northrup type K potentiometer. The Weston cell used as standard was several times compared with another cell tested by the Bureau of Standards. The hydrogen and calomel cells were kept in a Freas water thermostat regulated to $.01^{\circ}$, all measurements being made at 25.00° . No difficulty was experienced from the use of the water bath, and careful testing of the leads and electrical system indicated no electrical leakage sufficient to cause appreciable error in the measurements.

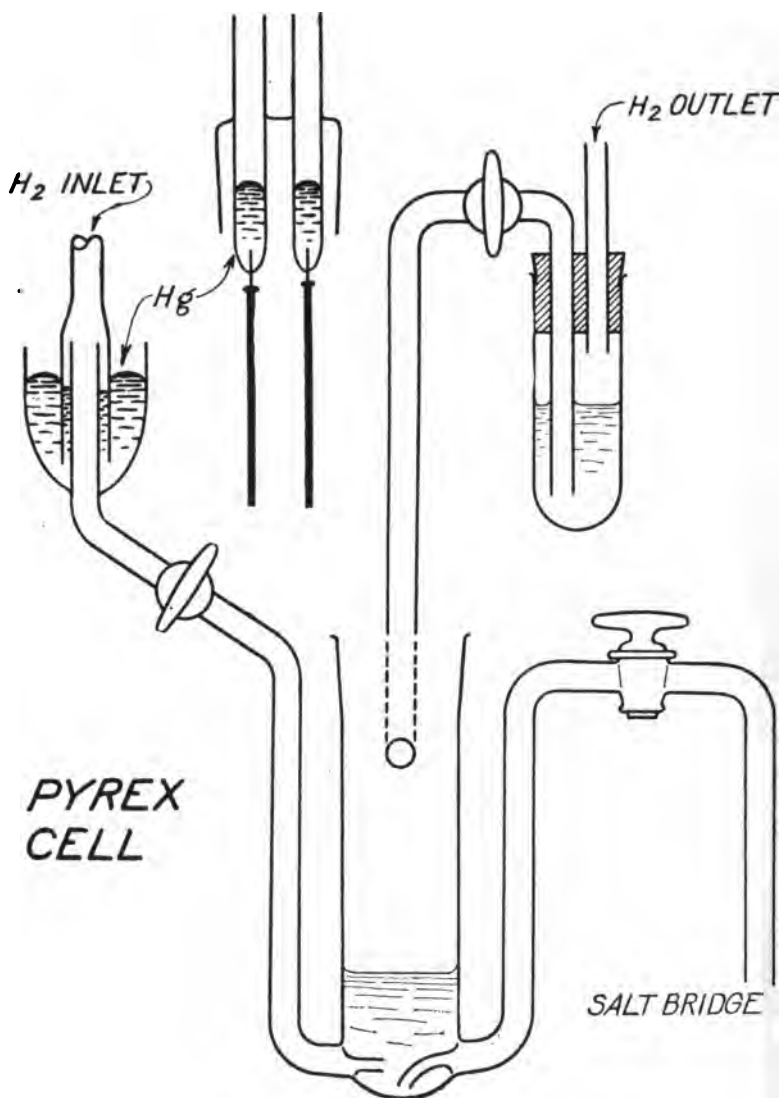
The saturated calomel cell as studied by Fales and Mudge² was used as standard electrode. Several different cells made up from different materials and at different times showed a maximum variation of 0.3 mv. Two calomel cells were always used, measurements being made against one which was frequently compared with the other. The hydrogen electrode vessel used is shown in Fig. I.

For cleaning electrodes use was made of a scrubber designed by Mr. Walden of this laboratory, which will be described in detail by him elsewhere. In the all-glass apparatus the vapors from boiling distilled water bubble through the

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water in which the electrodes are immersed, condense in a reflux, and fall back. An intermittent syphon on the Soxhlet principle removes the condensed water at intervals of five to ten minutes and allows a fresh portion to accumulate.

FIG. 1



The hydrogen was generated by electrolysis of a 15% sodium hydroxide solution. It was passed successively through a column of absorbent cotton, an electrically heated quartz tube containing platinized asbestos, a bead tower through which dilute sulfuric acid was continuously circulated by the passage of the gas, and a soda-lime tower. Such few rubber connections as were used were carefully wired and shellacked. The sulfuric acid and soda lime might seem superfluous were it not that small amounts of ammonia present in the hydrogen at one time in the course of the work were traced back to a little nitrate or nitrite (diphenylamine test) in the generator electrolyte. Since the original sodium hydroxide gave no such test the only obvious source is nitrogen compounds in the nickel electrodes, the work of Fichter and Suter³ having made electrolytic oxidation or reduction of atmospheric nitrogen very unlikely.

The water used throughout this investigation was prepared in the conductivity water still in use in this laboratory, which is similar to that described by Bourdillon⁴, and was kept in a protected quartz vessel.

Some of the potassium chloride was recrystallized three times from conductivity water in platinum and heated just below the fusion point. Since it was found that other factors, particularly contamination from glass vessels, were more important than the purity of the potassium chloride; and since this research was concerned with the development of the hydrogen electrode and not with absolute measurements in pure potassium chloride solutions, the final measurements were made with potassium chloride which was only once recrystallized with centrifugal drainage and washing.

Values for the combination:

Hg — HgCl sat. KCl — 0.1 M. HCl — H₂ — Pt

at one atmosphere total pressure have been obtained varying from 0.3080 to 0.3120 volts as compared with the 0.3100 of Fales and Mudge². Since the calomel cells showed so little variation, and since the potential difference between any active hydrogen electrodes in the same solution of 0.1 M. HCl is unmeasurably small it seems reasonable to assign the variability of this cell to the contact between the two solutions.

This conclusion is supported by the fact that age of the junction, mechanical mixing, and particularly bore of tubing in which the junction is made exert a great effect upon the potential of the combination. It perhaps deserves notice that this cell, although it has a small temperature coefficient ², is sensitive to sudden changes in temperature.

Electrolytic Deposition of Platinum.

Although massive platinum can be given a temporary activity as a hydrogen electrode, all practicable electrodes are coated with electrolytically deposited metal (iridium and palladium have also been used). The usual electrode has been coated with finely divided so-called platinum black, and it has generally been assumed that a smooth, velvety, continuous coating is desirable. To obtain this the Lummer-Kurlbaum method of adding a trace of lead salt to the platinizing solution is frequently recommended and as frequently denounced as harmful ⁵. A black deposit may often be obtained from commercial chlorplatinic acid, and Kohlrausch suspected that differences in the quality of the deposit with different samples of chlorplatinic acid are due to traces of impurities. To settle the point a solution of chlorplatinic acid was purified by three precipitations of ammonium chlorplatinat ⁶. The material thus obtained gave a dull gray deposit but not a black at high current densities and with frequent reversals of the current. With a current of 2 milliamperes per sq. cm. a smooth bright deposit was obtained on a gold base. Since therefore some impurity is necessary to obtain a black deposit, there can be little objection to the conscious addition of a trace of lead ion.

For the deposition of platinum black from a solution of chlorplatinic acid containing a trace of lead ion, current density and concentration of chlorplatinic acid are of minor importance, except that with very dilute solutions stirring becomes necessary. Reversing the direction of the current at intervals seems to have little effect, but the current should always pass in the direction of cathodic polarization for some time at the end of the process if commutation is used. If the final treatment is anodic the reduction of the oxidation products formed requires so much time that the electrode is slow in coming to equilibrium.

Aside from the use of an acid solution of purified chlorplatinic acid, we have obtained bright platinum deposits by the use of alkaline solutions of the purified chlorplatinic acid. The addition of sodium hydroxide to a solution of chlorplatinic acid has no immediate apparent effect. Within the course of a few days a brown precipitate forms, which gradually increases. The platinum is not however completely precipitated after one and a half months at ordinary temperature. This precipitate does not interfere with the use of the solution for plating and is in any case easily dissolved by adding hydrochloric acid and heating. Alkaline solutions containing lead ion give, however, a black deposit. Excellent results have also been obtained with the frequently recommended alkaline citrate bath, but the bright electrodes used in this work have been plated from alkaline solutions containing no citrate, since it was felt that the decomposition products of the citrate offered an additional source of contamination of the electrode.

The Role of Platinum and the Effect of Oxygen.

The early workers on the gas cell discovered that more reproducible and better results with hydrogen electrodes were obtained when the electrodes were coated with platinum black than when massive platinum was used. Ostwald⁷ pointed out the role of platinum black as a catalyst for the reaction



but emphasized that all electrodes must give the same potential provided the reaction consists only in solution or deposition of hydrogen, that is that the electrodes are truly inert; and that equilibrium is obtained. There have been only few references⁸ to the marked difference in potential between bare and platinized electrodes, and no explanation. Yet previous investigators have assumed that hydrogen electrodes must be coated with finely divided platinum; varied by some by the use of palladium or iridium, and by the use of gold instead of platinum as a base.

That the essential function of the platinum black is that of a catalyst for the electrochemical reaction,



is perhaps implicit in much of the discussion of the subject,

and has been specifically mentioned by G. N. Lewis⁹. The curves in Figs. 2 and 3 make this function particularly clear.

FIG. 2

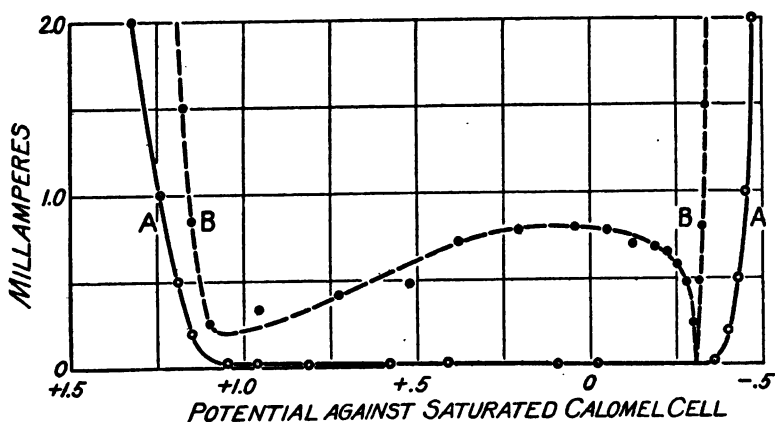
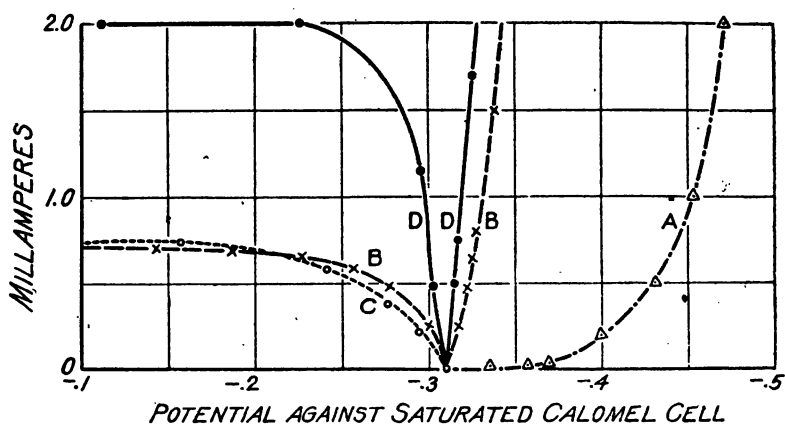


FIG. 3



These are anodic and cathodic polarization curves for 1 cm. square platinum foils in tenth molar hydrochloric acid saturated with hydrogen and stirred by a rapid hydrogen stream. The polarization potentials were measured against the saturated calomel cell during the passage of the polarizing current;

and since anode and cathode were separated only by 1 cm. the potential drop due to the resistance of the solution was neglected. Curves A and B in Fig 3 are the same as curves A and B of Fig. 2, but on a larger scale of abscissae. Polarization curves for hydrogen electrodes have been made before¹⁰, but the particular comparison made here is, it is believed, new.

Curve A is for a freshly ignited platinum foil, curve B for the same foil heavily coated with platinum black. The interesting passivity phenomena first noted by Sackur are well exhibited, but the important thing is the very great ease with which hydrogen deposits or dissolves on a platinized electrode as shown by the steepness of the curves and the small polarization. The ideal state of thermodynamic reversibility is rapidly approached as the rate of the reaction decreases. On a bare electrode there is on the contrary the considerable passive resistance to the deposition of hydrogen known as over-voltage, while on the side of anodic polarization, very small currents flow which continually decrease after each increase in polarization. At least a part of the current is certainly charging current (Ladungsstrom), and whether any of it is due to the reaction



is well open to doubt

The function of the platinum black is then that of a catalyst. That massive platinum can become a powerful catalyst for the combination of hydrogen with oxygen was noted by Faraday¹¹. One of the methods used by him to produce this "activation" was anodic polarization. In this connection curve C in Fig. 3 shows the anodic polarization curve for the foil used in curve A after it had been subjected to anodic polarization sufficient to evolve oxygen. The cathodic curve is practically coincident with curve B. Curve D in Fig. 3 shows the polarization curves for the same platinized electrode that was used for curve B but was taken immediately after a powerful anodic polarization. Anodic polarization produces in a solid platinum foil a catalytic activity for the solution or deposition of hydrogen practically as great as that of a platinized foil of the same size which has been in use for

some time. Anodic polarization markedly increases the activity of platinized electrodes.

Massive platinum activated in this fashion should then be capable of acting as a hydrogen electrode and offers obvious advantages of cleanliness as compared to platinum black. A number of experiments were carried out with various periods of polarization using hydrochloric acid, potassium chloride, sodium sulfate, and sodium hydroxide as electrolytes for the polarization. The activation was however found to be of too temporary a nature to permit the preparation of useful electrodes in this fashion. The results when such oxidized platinum electrodes were compared with platinized electrodes in tenth molar hydrochloric acid were uniformly as follows: The electrode showed at first an oxidizing potential 1.2 to 1.3 volts positive to the platinized electrode. This lasted from 15 minutes to several hours, when a very rapid change brought the potential almost if not quite to that of the platinized electrode. Following this was a slow change in potential toward the positive side so that after an hour or two in a hydrogen atmosphere the electrode did not behave materially different from one not activated. It should be emphasized that, while treatment with hydrogen soon destroyed the activation, long standing in water exposed to the laboratory atmosphere or thorough washing did not do so. Chemical oxidizing agents such as aqua regia, chlorplatinic acid, or chromic acid mixture gave a temporary activation similar to that produced by electrolytic oxidation.

The bright electrodeposits of platinum obtained from acid or alkaline solutions of purified chlorplatinic acid and from alkaline citrate solutions possessed activity in a high degree and with an effective life that made possible the use of this method for preparing electrodes. The deposits from alkaline chlorplatinate solutions were studied thoroughly from the point of view of their applicability to measurements on unbuffered solutions.

A factor in the use of the hydrogen electrode which does not seem to have received proper consideration is the effect of oxygen. The results obtainable with the Hildebrand type of bubbling electrode and the speed with which the hydrogen

electrode potential is attained after hydrogen is started bubbling through a solution originally saturated with air furnish convincing evidence that the sensitiveness of the hydrogen electrode to traces of oxygen may well be small. Certain qualitative observations made in the course of the other work suggested that this factor might repay careful investigation.

The method used consisted in fusing a bulb containing sodium hydroxide solution and furnished with two platinum electrodes on to the hydrogen system. A measured current was passed through this to develop a mixture of oxygen and hydrogen; and by comparing the current in the hydrogen generator and in this auxiliary generator the proportion of oxygen in the hydrogen entering the cell could be determined. The following table contains the results, two electrodes being used simultaneously, and the gas passing at a rate of 2.5 liters per hour.

Gold wire electrodes with bright platinum plate from alkaline chlorplatinic solution. Phosphate buffer solution of potential .6356 against the saturated calomel cell. $\frac{1}{2}$ — $1\frac{1}{2}$ hours after hydrogen flow started.

% O ₂		.009	.043	.086	.215	.43
Potential change	} No. 1	.02	.14	.44	1.3	3.5
in millivolts		No. 2	.02	.17	.53	1.5

Same $4\frac{1}{2}$ —5 hours after start.

% O ₂					.043	.086
Potential change	} No. 1	-	-	-	.44	1.0
in millivolts		No. 2	-	-	.51	1.1

Same 20—21 hours after start.

% O ₂				.009	.045	.091
Potential change	} No. 1	-	-	.06	1.3	2.8
in millivolts		No. 2	-	.10	2.0	4.0

Electrodes removed to water saturated with air for 1 hour. $1\frac{1}{2}$ —2 hours after return to H₂.

% O ₂				.009	.045	.091
Potential change	} No. 1	-	-	.01	.5	1.4
in millivolts		No. 2	-	.01	.6	1.6

Same 19—20 hours later. Total period in H₂ 44 hrs.

% O ₂				0	.01	.048
Potential change	} No. 1	-	-	-	.3	.9
in millivolts		-	-	-	.6	1.9
	} No. 2	-	-	-	.6	1.9
		-	-	-	.6	1.9

Same gold wire electrodes coated with platinum black.
Same solution. ½—1 hour after start.

% O ₂			.009	.045	.09	.22	.90
Potential change	} No. 1		.00	.02	.05	.27	1.5
in millivolts			.00	.02	.05	.32	1.6
	} No. 2		.00	.02	.05	.32	1.6
			.00	.02	.05	.32	1.6

Same 6 hours after start.

% O ₂						.045	.22
Potential change	} No. 1	-	-	-	-	.09	.9
in millivolts		-	-	-	-	.09	1.0
	} No. 2	-	-	-	-	.09	1.0
		-	-	-	-	.09	1.0

Same 24 hours after start.

% O ₂					.047	.094	.24
Potential change	} No. 1	-	-	-	.4	1.4	3.1
in millivolts		-	-	-	.4	1.8	3.6
	} No. 2	-	-	-	.4	1.8	3.6
		-	-	-	.4	1.8	3.6

Same 47 hours after start.

% O ₂						.047	.094
Potential change	} No. 1	-	-	-	-	2.	5.
in millivolts		-	-	-	-	3.	6.
	} No. 2	-	-	-	-	3.	6.
		-	-	-	-	3.	6.

Same after 1½ hours in water saturated with air; ¾ hour after return to cell.

% O ₂						.047	.094
Potential change	} No. 1	-	-	-	-	.5	1.9
in millivolts		-	-	-	-	.5	1.9
	} No. 2	-	-	-	-	.5	1.9
		-	-	-	-	.5	1.9

Same after total of 117 hours in hydrogen.

% O ₂						.047	.24
Potential change	} No. 1	-	-	-	-	4	14
in millivolts		-	-	-	-	5	14
	} No. 2	-	-	-	-	5	14
		-	-	-	-	5	14

Electrodes with fresh platinum black. Same phosphate buffer ½—1½ hours after start.

% O ₂			.046	.091	.23	.91
Potential change	} No. 1	-	.03	.13	.25	.7
in millivolts		-	.03	.13	.25	.7
	} No. 2	-	.03	.13	.25	.7
		-	.03	.13	.25	.7

Same electrodes in 0.1 M. HCl. Total period in hydrogen, 2½—3 hours.

% O ₂					.046	.23	.91
Potential change	} No. 1	-	-	-	.00	.01	.28
in millivolts		} No. 2	-	-	-	.00	.01

Freshly platinized electrodes in 0.1 M. HCl. 1—2 hours after start.

% O ₂					.046	.23	.91
Potential change	} No. 1	-	-	-	.00	.00	.12
in millivolts		} No. 2	-	-	-	.00	.00

Freshly platinized electrodes in 0.0998 M. KOH purified through the amalgam. Potential .9995 against saturated calomel cell. 1½—2 hours after start.

% O ₂					.0091	.046
Potential change in millivolts	} No. 1	-	-	-	2.7	17
		} No. 2	-	-	-	3.0

Same electrodes in phosphate buffer. ½—1 hour after start.

% O ₂					.046	.23
Potential change	} No. 1	-	-	-	.28	3.3
in millivolts		} No. 2	-	-	-	.38

It is evident from these data that both for black and for bright electrodes the resistance to the effect of oxygen decreases as the time of exposure to hydrogen increases. Indeed the limiting factor upon the use of electrodes is the sensitiveness to oxygen which finally becomes so great that no reasonable precautions can give correct results. It is perhaps not realized how rapidly oxygen can diffuse through an unlubricated ground joint even against a slight pressure of hydrogen.

To a certain extent the sensitiveness to O₂ which develops on long action of hydrogen may be reduced by removal from the hydrogen and subjection to the action of atmospheric oxygen. It should be pointed out that this effect is in no way a matter of age, but depends upon the action of the hydrogen itself. In the course of this work bright electrodes were kept in a sodium hydroxide solution in a closed dessicator for one month after plating and then gave satisfactory results in continuous use in a hydrogen atmosphere for five days. Other

electrodes have stood in water exposed to the laboratory atmosphere for days without material injury.

The sensitiveness to oxygen is markedly a function of the hydrogen ion concentration of the solution being least in strongly acid, and greatest in strongly alkaline solutions. The extremely small effect—0.12 mv. produced by 0.91% oxygen under the most favorable conditions of freshly platinized electrodes in tenth molar hydrochloric acid is at least as striking as the enormous effect noted in strongly alkaline solutions.

Aside from the difference in the relative solubilities of the gases which would tend to enrich the solution relatively to the gas phase in oxygen, it does not follow that the solution in the immediate neighborhood of the electrode contains anything like the proportion of oxygen indicated by the composition of the entering gas. In other words the change in the potential produced by a given per cent. of oxygen in the entering gas may be an inverse measure of the catalytic power of the electrode in accelerating the combination of hydrogen and oxygen.

In this direction the present work is in complete agreement with the results of Hofmann and his co-workers¹², who studied directly the rate of combination of mixtures of hydrogen and oxygen in the presence of aqueous solutions and under the influence of platinum metal catalysts. They found that previous treatment with oxygen increased, previous treatment with hydrogen decreased the catalytic activity; and that the activity was greatest in strongly acid solutions, smaller in bicarbonate solutions, and almost negligible in tenth molar potassium hydroxide solution.

An aspect which is frequently mentioned in discussions of the hydrogen electrode is the time required to come to equilibrium, for which the oxygen effect just mentioned is undoubtedly of importance. But it has been the general experience in the present work that such factors as design of cell and rate of hydrogen flow are of immensely greater importance in this respect than the properties of the electrode. This is in entire agreement with the results of Dolezalek²¹, who related the influence of these factors to efficiency of saturation with hydrogen. The present work would lay the empha-

sis rather on efficiency of removal of oxygen by combination with the hydrogen.

As already mentioned the potential of the hydrogen electrode depends upon the electrochemical reaction



and two inert electrodes in the same solution saturated with hydrogen should exhibit a zero potential difference if this is the only reaction taking place and if equilibrium is attained. It will be shown later that differences in potential between hydrogen electrodes in unbuffered neutral solutions are due to contamination of the solution by the electrode, that is to differences in composition of the solution in the immediate neighborhood of the different electrodes.

But there are other sources of potential difference between platinum electrodes in a solution saturated with hydrogen. For instance a bare platinum electrode is positive toward a similar platinized foil in the same solution of tenth molar hydrochloric acid saturated with hydrogen, and it was believed worth while to investigate this phenomenon. The potential difference may be anything up to about 0.3 volts. It persists over long periods of time⁸. In order to prevent any contamination with oxygen, bare and platinized electrodes were sealed into a cell, which was then filled with tenth molar hydrochloric acid and saturated with hydrogen. The cell was then sealed completely by fusing off hydrogen inlet and outlet. The catalytic power of the platinized electrode should make complete the combination of any traces of oxygen. The following is the history of such a pair of electrodes. After saturation with hydrogen for one hour the potential difference was 8 mv. The cell was then sealed and the potential read immediately and found to be 7 mv. Five minutes later it was 6 mv., twelve hours later, 4 mv., and from then on the course was as follows:

Days	2	4	18	21	26	30
Potential diff. (mv.)	64	202	47	42	42	77

If a platinized and a bare electrode are arranged in a cell with tenth molar hydrochloric acid in a continuous hydrogen current so that the potential against a calomel cell may be measured, and the two electrodes are connected by a metallic

conductor, the potential of the combined electrodes is, as quickly as a measurement can be taken, the same as that of the platinized electrode alone. The point is important in view of the prevalent idea that the time required for a hydrogen electrode to come to equilibrium depends upon saturation of the electrode with hydrogen and that therefore a gold plated base is to be preferred to solid platinum. In this connection it may be mentioned that the present investigators have been unable to prepare gold plated platinum in which there were no pin holes or blisters revealed by slight polishing.

When the electrodes are connected a small current flows which drops off rapidly if they are directly short circuited to negligible values. On removal of the short circuit, the potential difference re-establishes itself. In another sealed cell showing a potential difference of 260 mv. a short circuit was established for five minutes. Immediately after opening the circuit the potential was 23 mv., five minutes later, 175 mv. The circuit was then closed for 16 hours. Immediately after opening the potential was 3 mv., 24 hours later 144 mv., 4 days later the potential was 105 mv. The circuit was closed 7 days. On opening the potential immediately was 37 mv., 3 days later 156 mv., 8 days 115 mv., and 12 days 77 mv.

The potential against the saturated calomel cell of a platinized electrode in tenth molar hydrochloric acid in a hydrogen atmosphere is -0.3100 volts; of a bare platinum electrode -0.1 to -0.2 volts. In a solution saturated with air the potential of a platinized electrode ranges around $+0.49$ volt, of a bare (freshly ignited) electrode around $+0.45$ volt. That is in a hydrogen atmosphere a bare electrode is less negative, in an oxygen atmosphere less positive than a platinized electrode. This would seem to dispose of the possibility that any reaction in which the metal of the electrode is concerned is the major source of the potential difference.

Of the theoretical questions raised by these results, one of considerable interest is the source of the energy which may be obtained from the combination of active and inactive electrodes. Such a pair in a sealed vessel containing a solution saturated with hydrogen is evidently a system out of equilibrium, since energy may be drawn from it. There is every evi-

dence that the difficulty resides in the inactive electrode. It is probable that this potential difference is a phenomenon related to the small currents that can be forced through between inactive electrodes in a hydrogen atmosphere short of the potentials necessary for liberation of hydrogen and oxygen. That such currents below the decomposition potential are due to diffusion of a depolariser was first suggested by Helmholtz and later studied by Nernst. That this "Reststrom" in the present instance is a diffusion phenomenon seems however excluded by the nature of the conditions.

Whatever the nature of the process that furnishes the energy it is one which encounters great resistance and is extremely slow. This follows from the failure of short circuiting the two electrodes to produce equilibrium; and explains why a combination of active and inactive electrodes shows no measurable change in potential from that of an active electrode alone. The amount of current that can flow between the electrodes is too small to polarize the active electrode measurably. That the energy cannot arise from oxygen dissolved in the liquid follows from the experiments on completely sealed systems and that the electrode metal is not concerned follows from the comparison of the behavior of active and inactive electrodes in the presence of hydrogen and in the presence of oxygen. The obvious but not wholly satisfactory explanation is that the slow process in question consists in saturation of the electrode with hydrogen, in which case the possibility of obtaining electrical energy must lie in a lower resistance to the transfer of hydrogen from solution to metal by a roundabout route including the other electrode, just as electrical energy may be obtained from the solution of zinc in acid by the introduction of another metal having a lower hydrogen overvoltage. It is hoped to study these and related phenomena further.

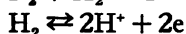
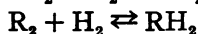
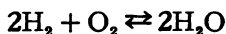
In this connection the well known fact that platinized and bare electrodes give the same oxidation reduction potential in such solutions as ferric-ferrous mixtures deserves mention. The Nernst conception of the oxidation-reduction electrode as a hydrogen or oxygen electrode has been sufficiently criticized on the theoretical ground of the extremely small or large hy-

drogen pressures concerned, but it may also be pointed out that there are serious difficulties in assuming a hydrogen electrode mechanism for the production of a reversible potential on a bare electrode which is incapable of acting as a reversible hydrogen electrode.

The activation of platinum electrodes by oxydizing agents and their deterioration under the influence of hydrogen is a very important question from the point of view of the whole subject of catalysis. The results obtained are in agreement with the work of Hofmann already mentioned and are confirmed by Willstätter's observation¹³ that in the catalytic hydrogenation of certain organic compounds by platinum black the catalyst loses its activity but regains it upon treatment with oxygen. This agreement between the results with oxygen and with organic compounds indicates that the essential factor is the hydrogen rather than the substance with which it reacts, and this is strongly confirmed by comparison of curves A and C in Fig. 3, where the catalysis of the simple reaction

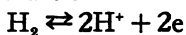


by platinum activated by oxidation is shown. The similarity in the behavior of the three reactions



is undoubtedly of significance from the point of view of the general theory of chemical reactions.

That the catalysis of the oxygen-hydrogen reaction is due to an oxygen compound of platinum rather than to platinum metal is a theory which has been much used in discussions of the subject¹⁴, and has even been applied by Willstätter to organic hydrogenations. That such an oxygen compound should be the catalyst for the reaction



with almost if not quite complete exclusion of oxygen seems much less likely.

That the inactivation is due to catalytic poisons present as impurities in the hydrogen but which are destroyed by oxidation is not completely excluded, but seems unlikely in view of

the attention given to the purity of the hydrogen used in the present work.

The suggestion that, whatever the nature of the combination, solution, or absorption of hydrogen by platinum, its properties are quite different when freshly formed than when aged, and that the function of the oxidation is to remove hydrogen previously present and clear the field for fresh combination was made by Hofmann; and he is responsible for the pertinent reference in this connection to the results of Harding and Smith¹⁵. These investigators found evidence in changes of resistance and length that hydrogen could exist in palladium as a transitional form which decreased the resistance and increased the length, and an alloy form which increased resistance but had little effect upon length.

Langmuir's experiments¹⁶ on the combination of hydrogen and oxygen on platinum surfaces were carried out under essentially anhydrous conditions and at very low pressures and the applicability of his conclusions to the present case is open to doubt. He suggests that the activation of the platinum produced by allowing the reaction to take place is due to a change in the nature of the surface; and this idea may possibly be adapted to the present case. Oxygen and particularly the strong oxidizing agents may loosen up the surface and increase its unsaturation, while hydrogen, if it actually dissolves in platinum, might well tend to increase the saturation of the surface, and bring it more to an equilibrium condition.

It is felt that the present results indicate the importance of the hydrogen electrode as a means for the study of the important subject of the so-called activation of hydrogen by platinum metals. It should be particularly valuable because it gives the effect on the hydrogen alone, whereas any method in which another substance reacts with hydrogen is open to the ambiguity that part of the effect may be exerted through the other reactant.

From the point of view of the practical use of the hydrogen electrode, this phase of the present work leads to the following conclusions:

Gold or gold plated platinum offers no advantage over

solid platinum as a base for hydrogen electrodes in point of time required for attainment of equilibrium.

In general the time required for attainment of equilibrium depends upon the efficiency of removal of oxygen; and is more a function of the design of the cell and the rate of hydrogen flow than of the properties of the electrode.

Electrodes deteriorate under the influence of hydrogen, becoming much more sensitive to traces of oxygen and finally unusable; but the process is partially reversed by exposure to oxygen.

Lack of attention to the complete exclusion of oxygen and the use of aged electrodes may produce no ill results on measurements in the acid or neutral range, but every care must be taken when the solution is strongly alkaline.

Wherever the nature of the solution permits, the platinized electrode is to be preferred to the bright plate because of lower sensitiveness to oxygen, and longer life.

Measurements in Unbuffered Solution.

The measurement of hydrogen electrode potentials in inorganic solutions which are strongly acid, strongly alkaline, or well buffered meets with little difficulty. In a neutral salt solution, however, the experience of the present investigators using the ordinary technique of the bubbling electrode gave a picture of absolute uncertainty—potentials changing rapidly up and down over wide ranges; wide differences in the potential of two electrodes in the same solution; and even differences in the direction of drift. This, moreover, with electrodes which agreed to within 0.02 mv. in tenth molar hydrochloric acid.

Lorenz and Mohn¹⁷ quote Nernst as saying that measurements in neutral salt solutions would give only "undefinierbare Potentiale." Clark¹⁸ states that, "There is hardly any use attempting the measurement of unbuffered solutions if indeed there would be any significance to the measurement if it were accurate." There should nevertheless be a difference in degree only between a measurement in tenth molar hydrochloric acid and one in millionth molar hydrochloric acid, or in pure water or in a potassium chloride solution. As to the theoretical importance and value of such measurements there

can be very little question. The electrical properties of pure water are, for instance, fundamental to the electrical properties of aqueous solutions.

The properties of platinum black are such that contamination of solutions to be measured by the electrode was to be expected and the conclusion has been reached in this work that it is futile to attempt measurements with the platinized electrode on unbuffered solutions in the neutral range. The active bright plated electrode already described was therefore developed, and with this it soon developed that the greatest single source of difficulty was the overwhelming tendency of platinum to occlude substances of an acid nature and to give up the occluded acid slowly but continuously. This property of platinum was observed by Faraday¹⁹ but deserves further emphasis. Aside from the universal tendency of electrodes prepared in an acid solution to exhibit a potential drifting toward the acid side, the following experiments may show the nature of the phenomenon.

A platinum foil one centimeter square was cleaned and ignited in the blast lamp. It was placed in conductivity water in the cell used for the measurements, and the liquid was stirred by a stream of purified hydrogen, or, in other experiments, of purified air. The results showed that one to one and a half hours was sufficient to make the water distinctly acid to methyl red, while without the platinum no such acidity developed. The platinum probably takes up sulfur trioxide from the gas flame²⁰.

A pair of electrodes plated in alkaline solution on a platinum foil base which had been cleaned by treatment with fused sodium hydroxide were thoroughly washed in the scrubber mentioned in the section on apparatus. They gave in a tenth molar potassium chloride solution potentials after 28 hours of .7290 and .7285 volts respectively, constant for 1½ hours. Used for a measurement in tenth molar hydrochloric acid lasting 26 hours they gave a potential of .3101 with variations from time to time of 0.1 mv., always, however, agreeing with each other within the precision of measurement. After four hours washing in the scrubber, they were placed in a fresh

portion of the same potassium chloride solution as before and gave the following values:

23½ hrs.	26½ hrs.
.6571	.6407
.6472	.6342

The only absolutely reliable method of removing this occluded acid seems to be treatment with fused sodium hydroxide. It is then the slow release of acid from the electrodes which accounts for the main part of the drift toward the acid side; for the failure of electrodes to agree, because electrodes in a solution of rapidly changing hydrogen ion concentration rarely agree; and for the sudden rapid changes in potential when the hydrogen flow is shut off, because the composition of the layer immediately next the electrode and hence the potential is a function of the rate of stirring.

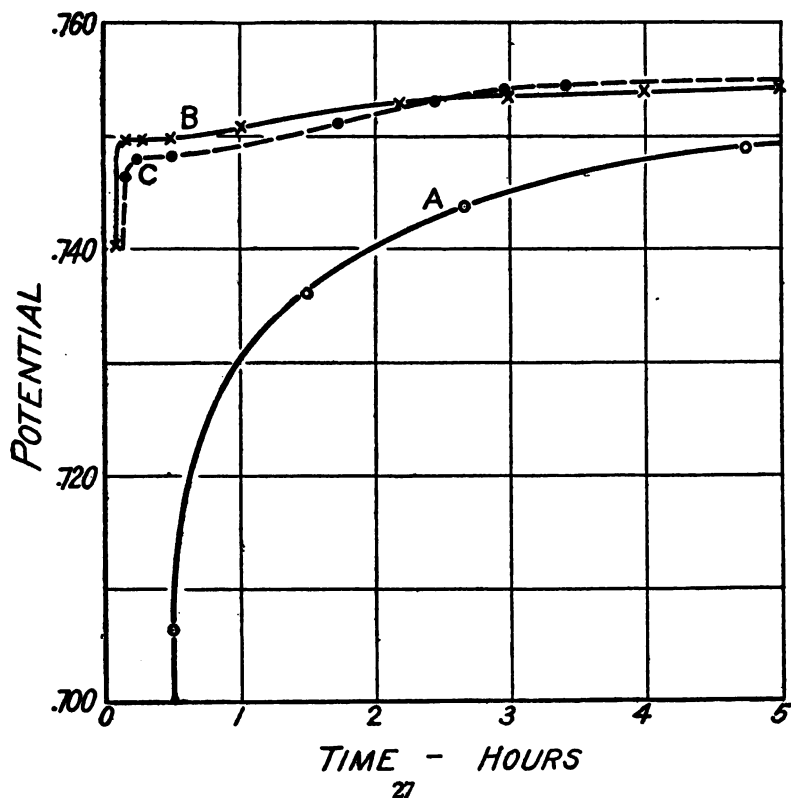
Gold wire electrodes coated with bright platinum from an alkaline solution were therefore used, and the greatest part of the drift toward the acid side was eliminated. The residual slow drift was explained by the discovery of electrical leakage across a porcelain base switch in the potentiometer circuit. This leakage, although barely detectable and much too small to affect the accuracy of the potentiometer measurement, allowed enough current to pass from calomel cell to hydrogen cell to increase the acidity of the latter. Disconnecting the leads from the cell except at the time of making the measurement removed this difficulty and electrodes were obtained whose agreement with each other and the steadiness of whose final potential left little to be desired.

Two possible objections remained. The time required to reach a steady potential varied from eight to twelve hours whereas a steady value is attained in buffered solutions in the same range in fifteen to thirty minutes. The final steady potential was in the neighborhood of .75—.77 volts, that is well on the alkaline side. These facts might be used to argue that there is contamination of the solution with alkali by the electrode in spite of the steadiness of the final equilibrium value and of the fact that successive runs on separate portions of solution with intermediate through scrubbing of the electrodes

showed no tendency to produce a less alkaline value in the second run.

The possibility that the slowness of attainment of equilibrium was due to the removal of carbon dioxide from the solution by the hydrogen stream was next investigated. It was found that immersion of the electrodes in the potassium chloride solution in the closed cell for 15 hours before starting the hydrogen had no marked effect upon the time required to come to equilibrium; but that bubbling hydrogen through the solution in the cell for several hours before introducing the electrodes had a very marked effect as may be seen from the curves in Fig. 4, where A is the curve of potential against time for a fresh solution, and B is for a solution previously thoroughly saturated with hydrogen.

FIG. 4



There still remained a drift of 8 to 10 mv. toward the alkaline side during the course of eight to ten hours after the first half hour which was considered to establish equilibrium as regards saturation and oxygen removal. That even this was due to atmospheric contamination was established by the following experiment. A pair of electrodes which had come approximately to equilibrium was removed from the cell into the atmosphere for thirty seconds and replaced. In Fig. 4 Curve B shows the potential time curve of the electrodes when removed directly from scrubber to the solution which had previously been thoroughly saturated with hydrogen; Curve C the corresponding curve after removal of the electrodes into the atmosphere for thirty seconds and replacement in the cell.

For a large part of the development work and for the final measurements a stock solution of potassium chloride in conductivity water of a concentration of 0.0863 M. was used. This was kept in a well steamed Non-sol bottle. The alkalinity of the solution is accounted for by the following experiment:

To 200 cc. of the above solution was added 0.5 cc. of a $\frac{M}{1000}$ hydrochloric acid solution and the potential was found to be 610 mv. against the saturated calomel cell. After nine days standing in a well steamed Non-sol bottle the potential was found to be 704 mv.

Contamination of solutions with alkali even by resistance glass is thus seen to be a serious matter. In the pyrex cell used in these measurements which had been in constant use over a period of four months, being steamed out on an average two to three times a week, such contamination of a solution which is already slightly alkaline seems to be negligible, and in the Non-sol bottles the rate of drift slows down materially as the solution becomes more alkaline.

The following series of measurements may serve as examples of the sort of results that may be obtained.

1. Solution not previously saturated with hydrogen. Date 7/26.

Time (hours : minutes)	14:47	16:00	18:33	19:37	20:56
Electrode I.	.7507	.7512	.7506	.7514	.7510
Electrode II.	.7510	.7512	.7506	.7513	.7511
	24:15	38:46	39:55	41:00	
	.7514	.7527	.7519	.7518	
	.7514	.7523	.7519	.7514	

2. Freshly plated electrodes scrubbed 4 hrs. Solution treated with hydrogen 16 hrs. Date 8/22.

Time (hours : minutes)	0:10	0:32	0:56	2:00	4:26	6:23
Electrode I.	.7552	.7558	.7568	.7588	.7617	.7631
Electrode II.	.7552	.7556	.7568	.7588	.7617	.7631
	7:27	8:28	9:38	10:43	23:03	23:43
	.7637	.7638	.7636	.7635	.7636	.7634
	.7637	.7638	.7636	.7635	.7636	.7633

3. Same electrodes scrubbed 4 hrs. Fresh portion of same solution treated with hydrogen 23 hrs. Date 8/24.

Time (hours : minutes)	0:10	0:31	1:14	3:08	4:00
Electrode I.	.7564	.7595	.7616	.7644	.7652
Electrode II.	.7564	.7595	.7616	.7644	.7652
	6:02	8:48	10:46	11:46	
	.7668	.7685	.7685	.7688	
	.7668	.7685	.7688	.7691	

It should be noted in these typical measurements that the maximum variation between duplicate electrodes is 0.4 and that only with old electrodes which are particularly sensitive to traces of oxygen and more exposed to the chance of having become contaminated; that in Run 1 the maximum variation from the 15th to the 41st hour is 1.9 mv.; that while successive runs with the same electrodes in different portions of the same solution leave considerable to be desired in agreement, there is certainly no tendency for further scrubbing of the electrodes to reduce the alkalinity of the final potential.

Measurements have also been made on solutions made by adding small amounts of very dilute hydrochloric acid to the

stock potassium chloride solution. Such a run is given in the following table.

Fresh electrodes. Solution previously saturated with hydrogen.

Time (hours : minutes)	0:22	0:37	0:53	1:07	1:22
Electrode I.	.6075	.6073	.6063	.6057	.6053
Electrode II.	.6075	.6071	.6061	.6056	.6053
	1:52	2:22	2:54	3:22	3:54
	.6044	.6040	.6042	.6042	.6044
	.6042	.6039	.6038	.6040	.6041
	4:22	5:12	6:17	20:27	20:54
	.6046	.6050	.6057	.6304	.6315
	.6044	.6049	.6057	.6303	.6314

These results show that even as near the neutral point as a pH of 6.5 close agreement between duplicate electrodes may be obtained; that in slightly acid solutions the carbon dioxide effect is of much less importance; that in such solutions the potential reaches a maximum rapidly, then drops a few millivolts (this seems to be very general); and that this drop is followed by a slow but steady drift toward higher potentials. As for the drop from the maximum, which is in any case small, it should be noted that the electrode is transferred directly to the solution from the scrubber in which the water is, if anything, alkaline from the action on the glass and that adjustment to a new solution may well be slow. The increase in alkalinity which follows may very well be due to the glass of the cell. Such contamination, it is evident, is unmeasurable with solutions already slightly alkaline, but by analogy with the Non-sol bottles might well be much more serious in a neutral solution where in the volume used a change of one millivolt requires only 4×10^{-11} moles of H^+ or OH^- ion. The results obtained show it is felt that measurements in this range may certainly be relied upon to within a few millivolts. The whole behavior of these electrodes as contrasted with those prepared in acid solution indicates that there is no such occlusion of alkali by the platinum as there is of acid, but a final proof that there is absolutely no contamination by the elec-

trodes will call for silica apparatus and redistillation in a closed system protected from atmospheric contamination. This will of course also be necessary for the accurate determination of the hydrogen electrode potential of pure water and of pure potassium chloride solutions.

The method which has been found satisfactory for measurements in such solutions as these together with the necessary precautions is as follows: The electrodes, two of which were always used, were of gold wire 1.25 mm. in diameter of which about 1 cm. was immersed in the solution. About 3 cm. above the level of the solution these were fused to platinum leads which were fused through the mercury cups on the cap of the cell. The platinum was thus kept well away from the solution. The electrodes when new were cleaned with hot chromic acid mixture, heated to low red heat, then treated $\frac{1}{2}$ to 1 hour with fused sodium hydroxide. They were then plated in an alkaline chlorplatinate solution with a current of about 20 milliamperes for 5 minutes, the electrolyte being stirred mechanically. The thickness of the platinum deposit seems to have little effect upon the life of the electrode. When not in use the electrodes were kept immersed in about tenth molar sodium hydroxide solution. Immediately before use they were washed in the scrubber for one hour or more, the water in the scrubber having been previously well boiled, and then transferred as quickly as possible to avoid contamination to the cell which contained the solution to be measured and through which hydrogen was already bubbling. As already mentioned these electrodes are comparatively sensitive to oxygen; the ground joint in the cell cap must therefore be kept moistened with conductivity water and all stopcocks through which hydrogen passes must be well greased.

It is hardly safe to rely upon such electrodes for more than 24 hours continuous service in a hydrogen atmosphere, and deposition of new platinum on top of the old seems to give uncertain results. The old deposit may be removed with some loss of gold by treatment with hot aqua regia, after which the electrodes should be heated to incipient fusion, then treated with fused sodium hydroxide and replated as before.

The criteria for satisfactory measurements in solutions of

— this nature are as follows: agreement of two electrodes in the same solution; steadiness of potential over considerable periods of time; and potentials which are unaffected by variations in the rate of hydrogen flow or even its complete cessation. It cannot be emphasized too strongly that almost any ill to which hydrogen electrodes are subject affects two electrodes differently and that two electrodes in the same solution offer a most potent means of separating errors due to the hydrogen electrodes from errors due to other parts of the cell. If the electrodes are contaminating the solutions or if there are leaks which allow oxygen to enter the system, stopping the hydrogen flow and sealing the cell will produce a sudden sharp change in potential so that this is also a very valuable criterion.

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VITA

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